ACID-BASE TITRATION

PURPOSE

To determine the concentrations of two acids by acid-base titration.

SUMMARY

An acid-base titration is a method used to quantitatively determine an unknown acid or base (the analyte) concentration by neutralizing it with a known concentration solution (the titrant). The equivalence point of a titration can be indicated by either identifying the steepest point on the titration curve measured by a pH meter, or a color change of a pH indicator.

In this experiment, two systems will be examined, the titration of:

(1) Strong Acid by Strong Base System.

A hydrochloric acid (HCl) solution with unknown concentration will be titrated with a standard solution containing 0.100 M sodium hydroxide (NaOH).

Note: the unknown HCl concentration is close to the concentration of human stomach acid.

(2) Weak Acid by Strong Base System.

An acetic acid (CH_3COOH) solution with unknown concentration will be titrated with a standard solution containing 0.100 M sodium hydroxide (NaOH).

Note: the unknown CH_3COOH concentration is around ten times diluted to the concentration of a typical household vinegar.

THEORY

Dissociation Constant of Water

Aqueous solutions always contain both aqueous hydrogen and hydroxyl ions as a consequence of the auto-ionization of water:

$$\mathbf{2\ H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}}$$

The H^+ ion is immediately hydrated, linking with a second water molecule, (the conjugate base, in Lewis terms) becoming H_3O^+, the hydronium ion.

The Bronstead-Lowery definition of an acid is a substance that can donate a proton, H^+, to another species. In aqueous solution, therefore, a (B-L) acid is any substance that can increase the $H^+_{(aq)}$ concentration (by forming $H_3O^+_{(aq)}$ ions). Similarly, a (B-L) base is a substance that can accept a proton, and consequently, in aqueous solution, lowers the $H_3O^+_{(aq)}$ concentration, and raises the $OH^-_{(aq)}$ concentration.

In any aqueous solution, the $H_3O^+_{(aq)}$ concentration, and $OH^-_{(aq)}$ concentration are not independent, but are related by:

$$Kw = [H_3O^+_{(aq)}]\cdot[OH^-_{(aq)}] = 1 \times 10^{-14}$$

where the square brackets denote concentrations, in moles per litre (M). This relationship is only strictly true at 25°C, but is valid at any temperature near room temperature.

The pH Concept

The range of $[H_3O^+_{(aq)}]$ values is extremely wide, therefore a log scale is more convenient. "Power of hydrogen" or pH, is defined as:

$$pH = -\log[H^+_{(aq)}]$$

A pH of 7 corresponds to a neutral solution, including pure water, solutions which have a pH of less than 7 are referred to as acidic, and those with pH greater than 7 are basic. From the relationship between $[H_3O^+_{(aq)}]$ and $[OH^-_{(aq)}]$, a relationship between pH and pOH can be derived:

$$pH + pOH = 14$$

Acid-Base Titration :

The purpose of an acid-base titration is to determine the unknown acid or base concentration. At the equivalence point, for a monoprotic acid, monohydroxy base, the relationship is:

$$M_{(standard)} \cdot V_{(standard)} = M_{(unknown)} \cdot V_{(unknown)}$$

where: M is the molarity and V is the volume

For all neutralization reactions, the equivalence point, by definition, is where the number of moles of $H_3O^+_{(aq)}$ ions is exactly equal to the number of $OH^-_{(aq)}$ ions. For example, using sodium hydroxide (NaOH) and hydrochloric acid (HCl):

$$\mathbf{NaOH_{(aq)} + HCl_{(aq)} \rightarrow H_2O_{(l)} + NaCl_{(aq)}}$$

Since the NaOH, HCl, and NaCl are all completely dissociated in aqueous solution, the only net reaction is:

$$\mathbf{OH^-_{(aq)} + H_3O^+_{(aq)} \leftrightarrow 2\ H_2O_{(l)}}$$

This means that to determine the concentration of the unknown, the number of moles of ions in the standard must be accurately known, along with the volumes of both the standard and the unknown, and there must be some way of determining when the equivalence point has been reached.

For the first, a precisely known *volume* of standard is usually used. This volume in litres, multiplied by the concentration, gives the number of moles of ions used. This number will be exactly equal to the number of moles of ions ultimately neutralized in the unknown, regardless of whether the unknown is a weak of a strong acid.

Determination of the equivalence point is slightly more complex, and varies depending on whether the unknown is weak or strong. (NOTE: a strong acid or base is generally chosen as the standard; it is only the unknown that may be either weak or strong.)

Strong Acid - Strong Base Titration:

For strong acid - strong base titration, we use standard NaOH to titrate unknown HCl.

At equivalence, by definition, all the original acid has been consumed, and there is no excess titrant base present.

$$\mathbf{NaOH_{(aq)} + HCl_{(aq)} \rightarrow H_2O_{(l)} + NaCl_{(aq)}}$$

The two species present at the equivalence point are H_2O and NaCl. Since NaCl is neutral, (as is water!) there is nothing in solution to cause the pH to be in the acidic or basic range. The equivalence point of a strong acid/strong base titration occurs at **pH = 7**.

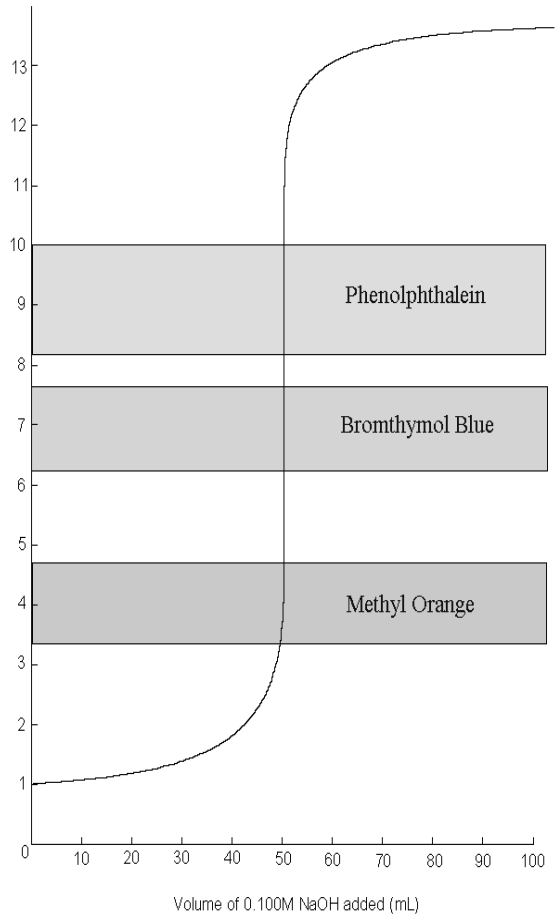
Weak Acid - Strong Base Titration:

For a weak acid-strong base titration, we use standard NaOH to titrate unknown CH_3COOH.

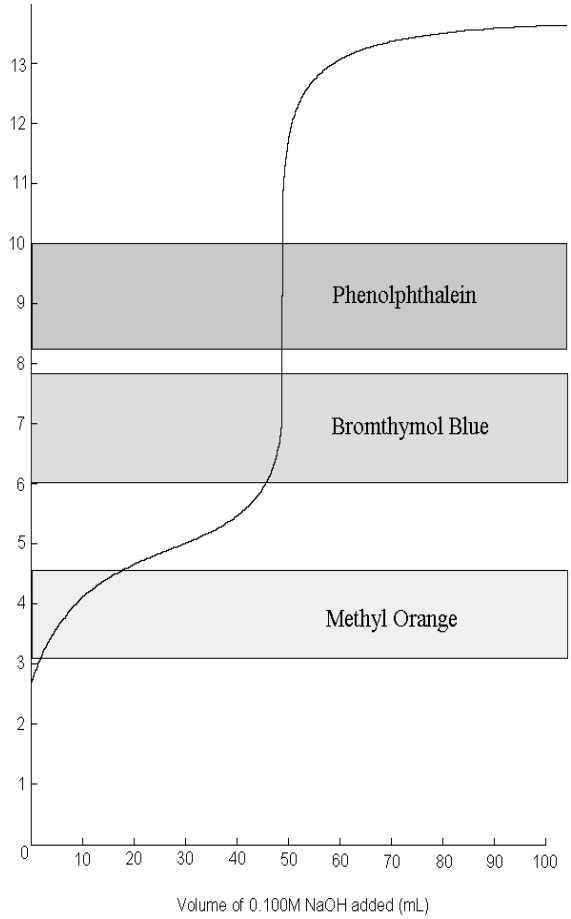
$$\mathbf{CH_3COOH_{(aq)} + NaOH_{(aq)} \leftrightarrow H_2O_{(l)} + CH_3COONa_{(aq)}}$$

The two species present at the equivalence point are H_2O and CH_3COONa. The equivalence pH is not 7 due to the presence of CH_3COONa, which is a (B-L) base. Remember that we mentioned before that a (B-L) base lowers the $H_3O^+_{(aq)}$ concentration and raises the $OH^-_{(aq)}$ concentration. **The pH at equivalence therefore is not 7**, but depends on the concentration of CH_3COONa.

TITRATION CURVES:



Strong Acid - Strong Base
(HCl – NaOH)



Weak Acid - Strong Base
(Acetic Acid – NaOH)

The indicator ranges for methyl orange (3.1-4.4), phenolphthalein (8.0-9.6) and bromthymol blue have been inserted in the graphs. For the strong acid-strong base titration, any indicator is suitable. But for the weak acid-strong base, the 'neutral' range of the methyl orange occurs before the equivalence point (approx. pH 9) is reached so that it would change colour much too soon. Thus it is important to choose the indicator so that it changes colour somewhere within the pH range spanned by the steep position of the curve.

Determining the Endpoint in Acid-Base Titration:

1. Using Indicators:

Acid-base indicators are complex organic compounds which change colour in solution as the pH changes (they themselves are weak acids or bases). By choosing an indicator whose colour change pH corresponds to a pH on the vertical portion of the titration curve for an acid-base

titration, the endpoint, as indicated by the indicator, will correspond to the equivalence point of the titration.

2. Using a pH Meter:

A pH meter is an instrument with an electrode that gives an electrical signal proportional to the $H^+_{(aq)}$ concentration in the solution in which it is immersed. The signal can be calibrated to give readings (on an analogue scale or as a digital read-out) directly in pH units. To locate the endpoint in acid-base titration, a pH meter will be immersed in the analyte solution, and record each pH change when the titrant is added. The endpoint is reached when the pH changes most rapidly with a small addition of titrant, which is the steepest point on the titration curve.

PRE-LABORATORY PREPARATION

SAFETY DATA SHEET (SDS)
Consult the online SDS databases found at:

www.google.ca with name of the chemical plus SDS

Sodium hydroxide, acetic acid, hydrochloric acid, phenolphthalein and methyl orange.

Please focus on "**Section 2 - Hazard(s) identification**", "**Section 7 - Handling and storage**".

PROCEDURE

Part A. Titration with a pH Meter

1. Ask your lab demonstrator if the pH meter is calibrated or not.

2. Obtain ~70 mL of "NaOH Standard (0.100 M)" in a clean 100-mL breaker.

3. Rinse the buret with ~10 mL of "NaOH Standard (0.100 M)". Discard the rinse into personal waste beaker.

4. Fill the buret with "NaOH Standard (0.100 M)", and let the top of solution sit a little more above the 0.00 mL level. Drain a small amount of solution into personal waste beaker so it fills the buret tip. Leave the solution right at the 0.00 mL level of the buret (the bottom of the meniscus sits on the 0.00 mL level).

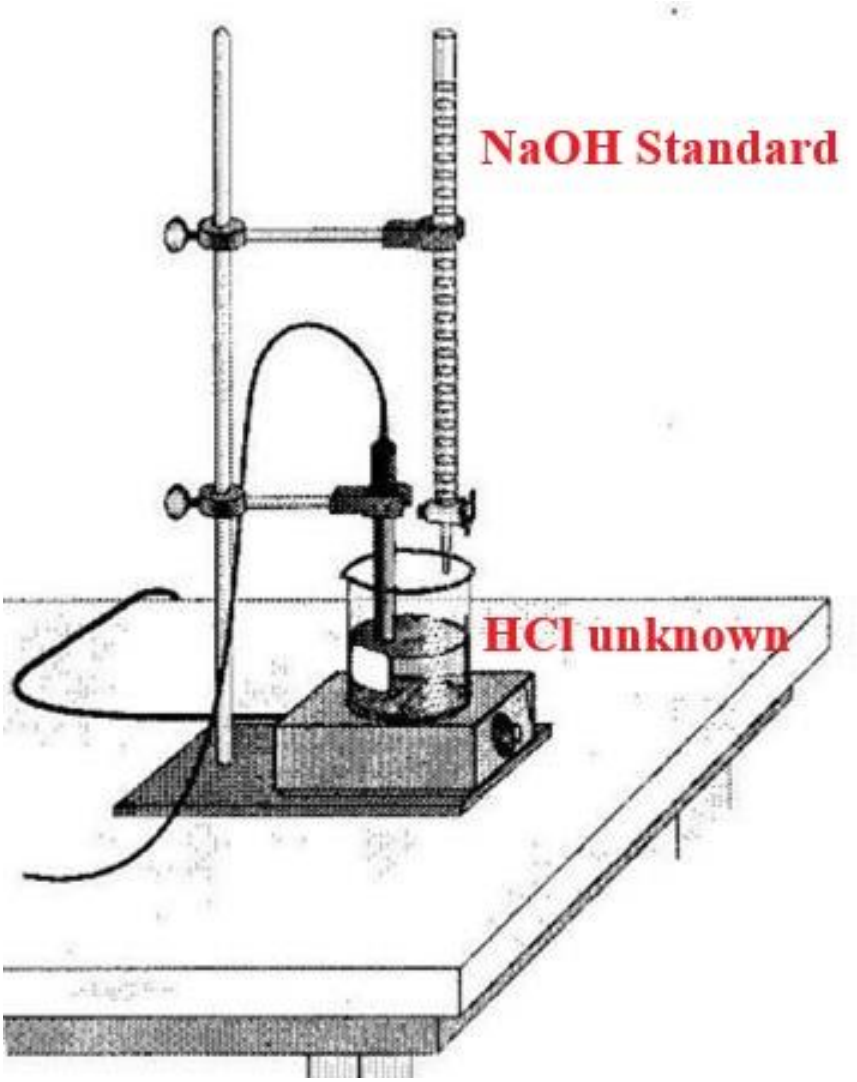
5. Obtain ~20 mL of "HCl unknown" in a clean 50-mL breaker. Rinse the transfer pipet with ~5 mL of "HCl unknown". Discard the rinse into personal waste beaker.

6. Pipet 10.00 mL of “HCl unknown” into a clean 250-mL beaker. Dilute it to about l00 mL with distilled water. Add a magnetic stirring bar to the solution. Place the beaker on a magnetic stirrer.

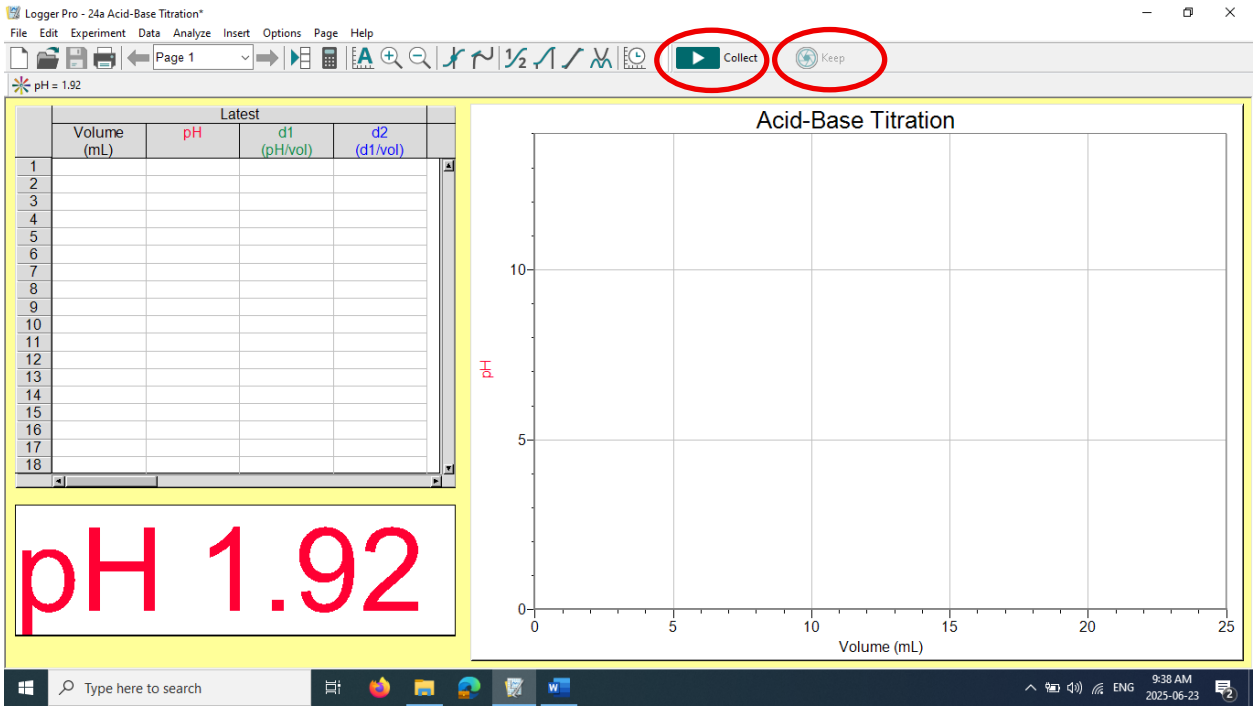
7. Remove the pH meter from the beaker of KCl. (Note: Never leave the pH meter stay dry in air. Place it in the beaker of KCl between measurements, and remember to wash it with distilled water before using). Rinse the pH meter with distilled water. Discard the rinse to personal waste beaker.

8. Immerse the pH meter into “HCl unknown”. Turn on the magnetic stirrer. Ensure gentle stirring without bubbling and the magnetic stir-bar cannot hit the pH meter.

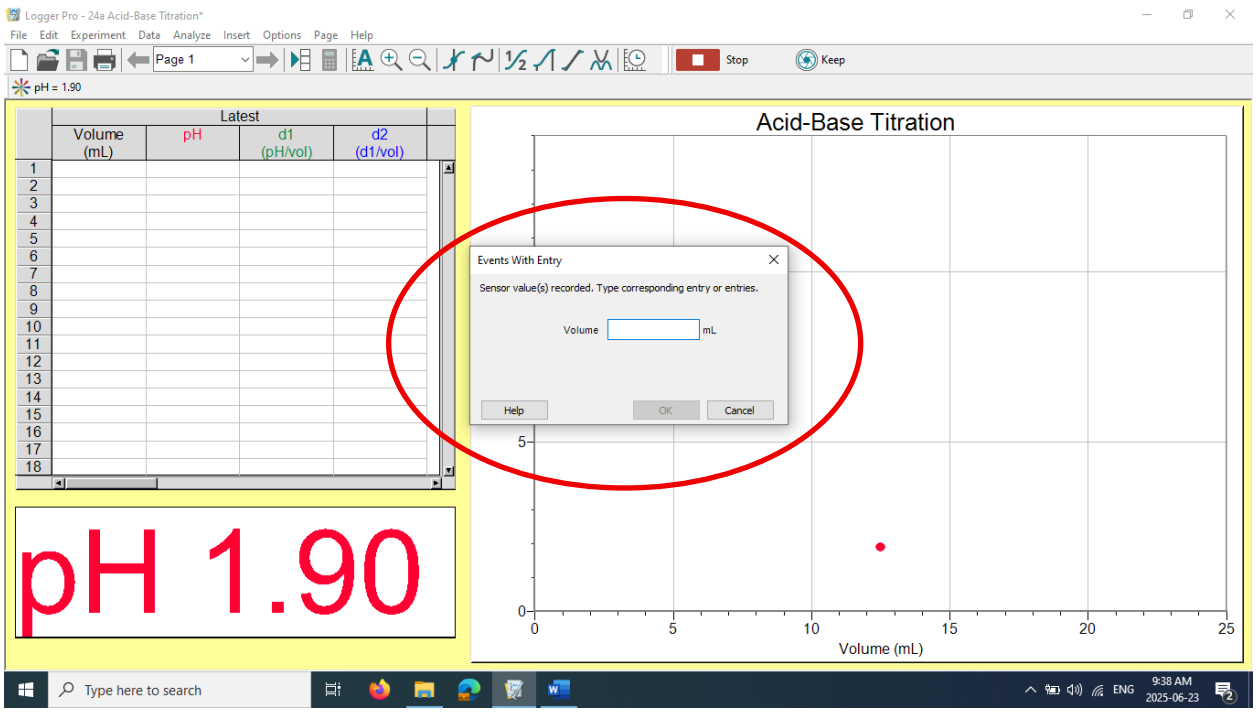
9. Set up the apparatus as the figure below. And ask your lab demonstrator to check.



10. On laptop, in the window of Logger Pro (see figure below), click "**Collect**". Once the pH value has stabilized, click "**Keep**".



11. In the edit box, type "**0.00**" and click "**OK**" (You enter "0.00" because 0.00 mL of NaOH has been added to solution). DO NOT PRESS STOP.



12. Slowly open the stopcock of the buret to add NaOH until the bottom of the meniscus sits on the 3.00 mL level. Wait for the pH value to stabilize. Once stable, click "**Keep**". In the edit box, type "**3.00**" and click "**OK**" (You enter "3.00" because 3.00 mL of NaOH has been added to solution).

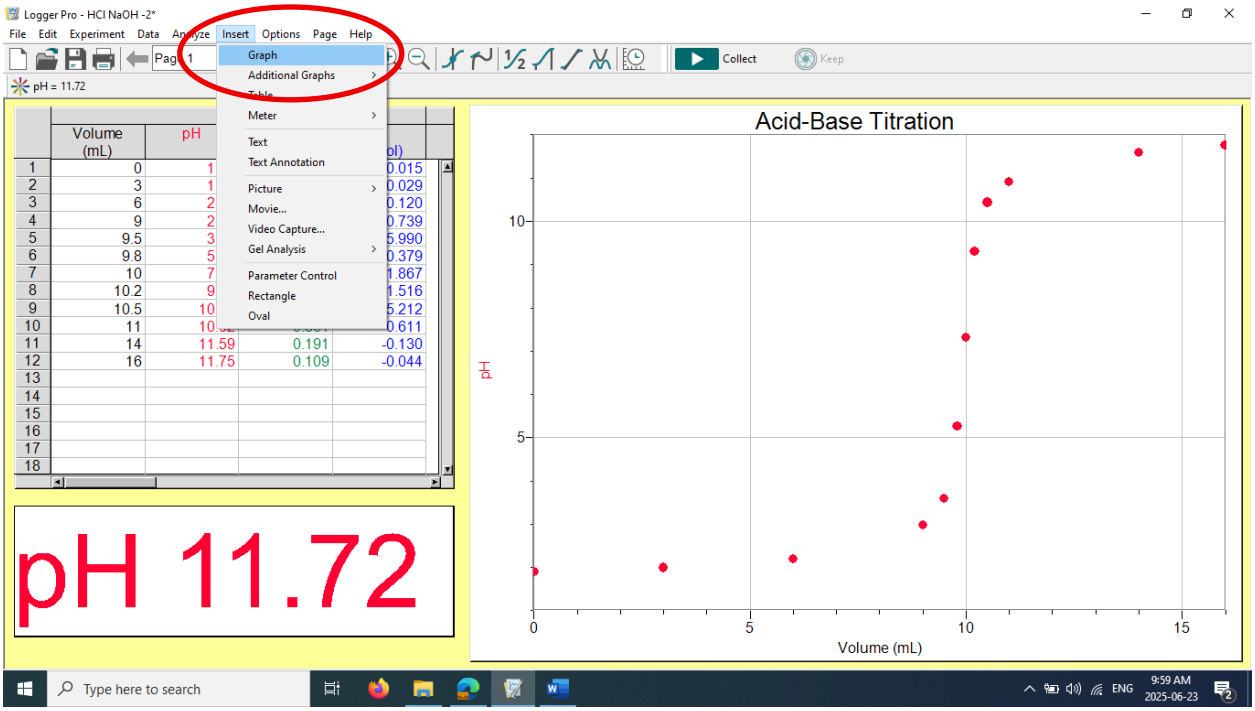
13. Slowly open the stopcock of the buret to add NaOH until the bottom of the meniscus sits on the 6.00 mL level. Wait for the pH value to stabilize. Once stable, click "**Keep**". In the edit box, type "**6.00**" and click "**OK**" (You enter "6.00" because 6.00 mL of NaOH has been added in total).

14. Repeat with successive additions of base until you approach the endpoint. As you are near the end point, decrease your NaOH increments. Continue adding NaOH until you have a full Acid-Base plot, and your pH no longer changes significantly with the addition of NaOH.

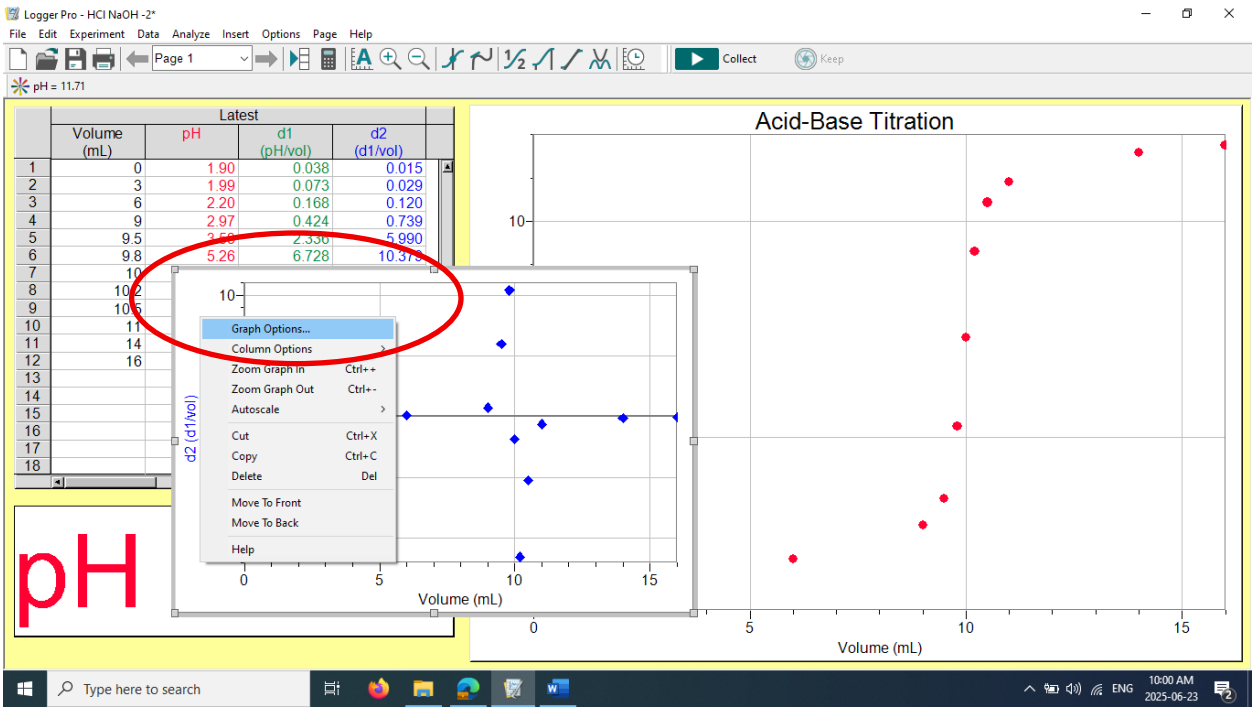
NOTE	You will use about 16 mL of NaOH in total. Here is the recommended amount of adding NaOH: 0.00 mL; 3.00 mL; 6.00 mL; **9.00** mL; **9.50** mL; **9.80** mL; **10.00** mL; **10.20** mL; **10.50** mL; **11.00** mL; **14.00** mL; **16.00** mL

9. Once you reach 16.00 mL, and pH value is stable, click "**Keep**". In the edit box, type "**16.00**" and click "**OK**". Then, click "**Stop**".

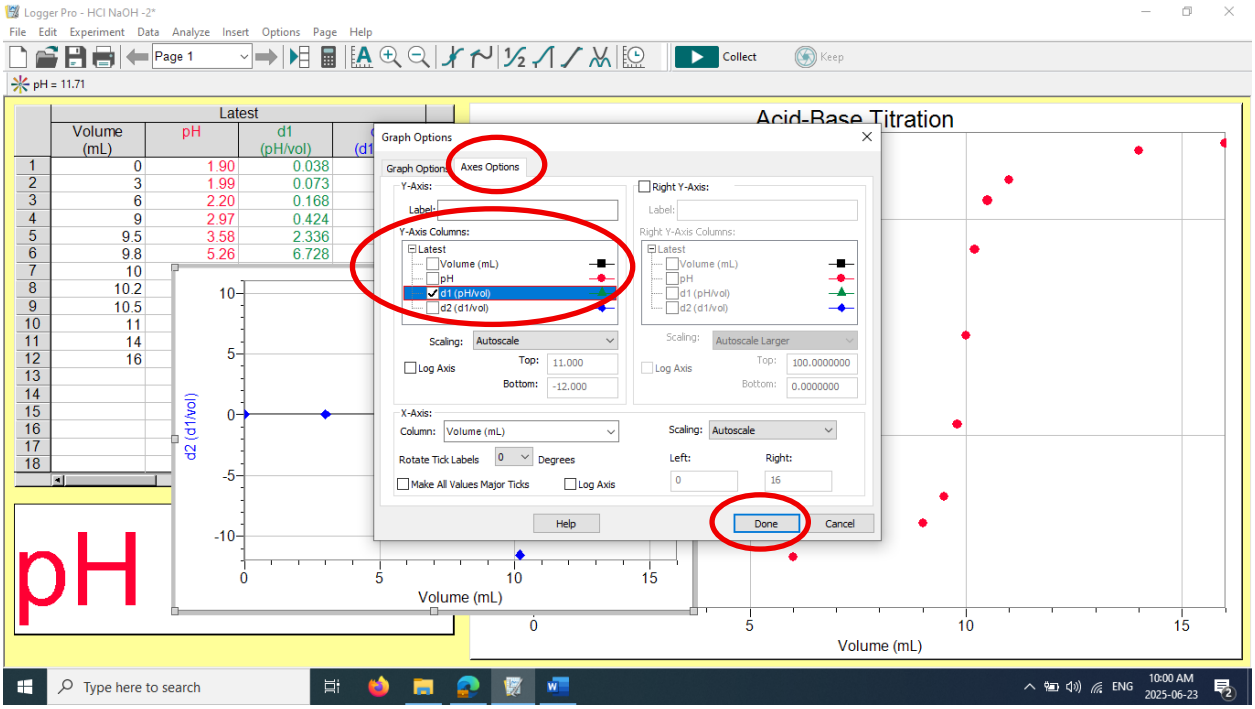
10. The steepest point on the titration curve gives the equivalence point. To find it, click "**Insert**", select "**Graph**".



11. A new graph window will pop up. Right click on it, select "**Graph Options…**".

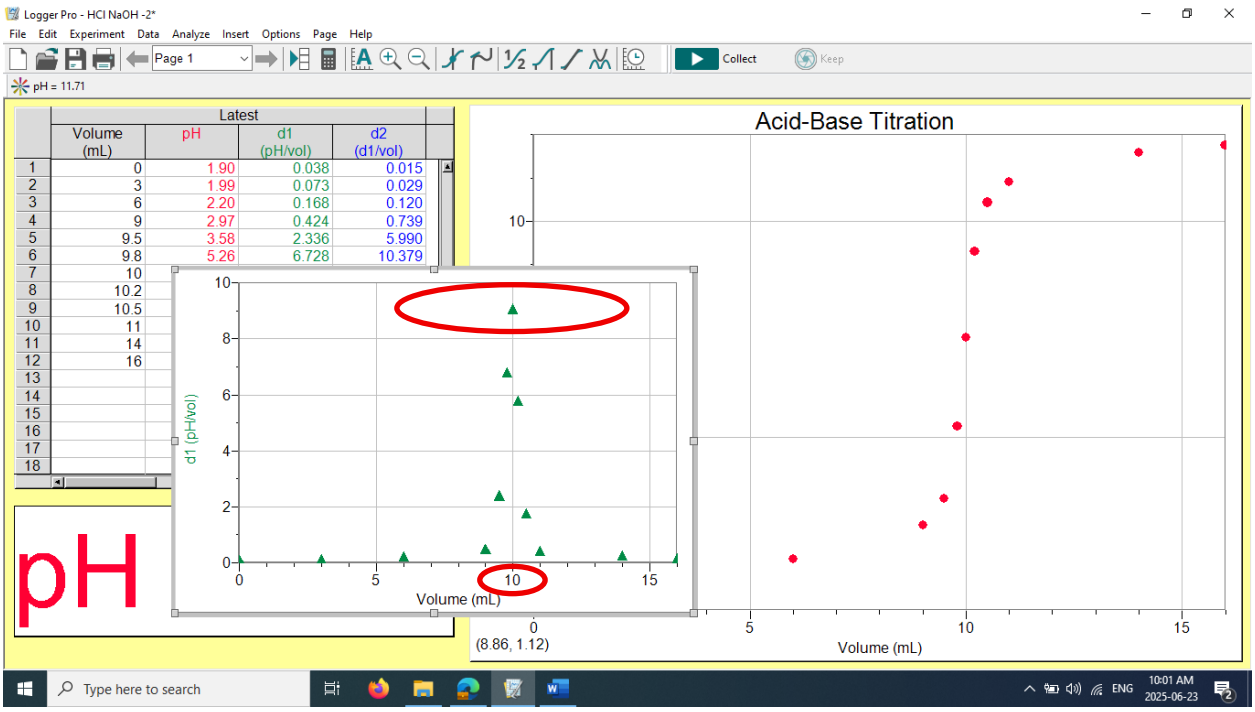


12. Go to "**Axes Options**", in the "**Y-Axis Columns:**", check only one box of "**d1(pH/vol)**", click "**Done**"



13. In the new plot, the highest data point is the equivalence point. The x value of this data point gives the titration endpoint volume of NaOH ($\mathbf{V_{(NaOH\ standard)}}$). For example, in the figure below, $V_{(NaOH\ standard)} = 10.00$ mL.

14. Press the "screen print" key to take a screen shot of your graph. Copy this graph into a word document. Save this document to the desktop.



15. Then, calculate the concentration of "HCl unknown":

$$M_{(NaOH\ standard)} \times V_{(NaOH\ standard)} = M_{(HCl\ unknown)} \times V_{(HCl\ unknown)}$$

Where $M_{(NaOH\ standard)} = 0.100$ mol/L
$V_{(HCl\ unknown)} = 10.00$ mL

$$0.100\ \text{mol/L} \times V_{(NaOH\ standard)} = M_{(HCl\ unknown)} \times 10.00\ \text{mL}$$

$$\therefore \boxed{\mathbf{M_{(HCl\ unknown)} = 0.100\ mol/L \times V_{(NaOH\ standard)} \div 10.00\ mL}}$$

For example, if $V_{(NaOH\ standard)}$=10.00mL, then $M_{(HCl\ unknown)}$=0.100×10.00÷10.00=0.100 mol/L

16. Repeat steps 2 to 15 using 10.00 mL "Acetic Acid unknown" instead of "HCl unknown".

B. Titration with a pH Indicator (phenolphthalein)

1. Obtain ~20 mL of "HCl unknown" in a clean 50-mL breaker. Rinse the transfer pipet with ~5 mL of "HCl unknown". Discard the rinse into personal waste beaker.

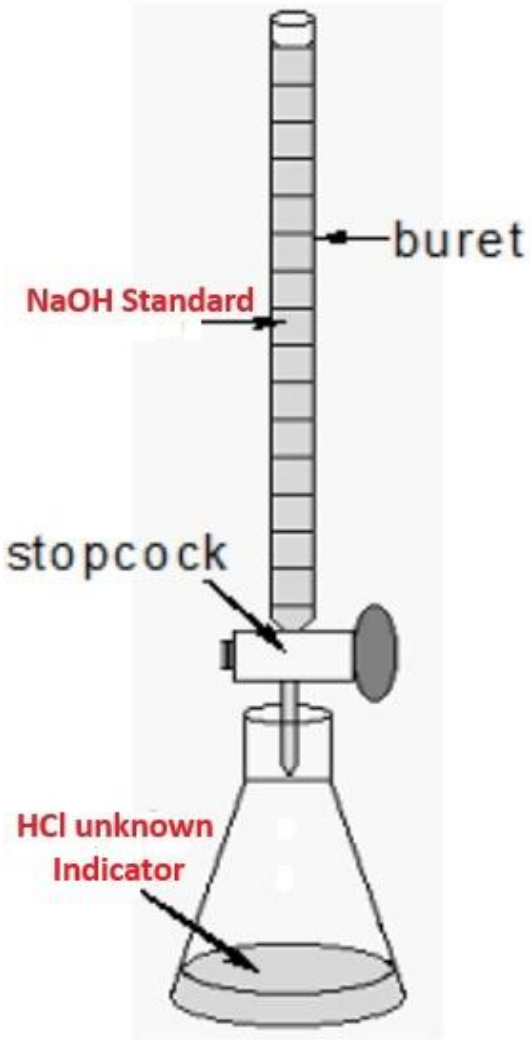
2. Pipet 10.00 mL of "HCl unknown" into a clean 250-mL Erlenmeyer flask. Dilute it to about l00 mL with distilled water. Add 3 drops of phenolphthalein. Swirl the flask for 10 seconds.

3. Obtain ~70 mL of "NaOH Standard (0.100 M)" in a clean 100-mL breaker.

4. Rinse the buret with ~10 mL of "NaOH Standard (0.100 M)". Discard the rinse into personal waste beaker.

5. Fill the buret with "NaOH Standard (0.100 M)", and let the top of solution sit a little more above the 0.00 mL level. Drain a small amount of solution into personal waste beaker so it fills the buret tip. Leave the solution right at the 0.00 mL level of the buret (the bottom of the meniscus sits on the 0.00 mL level).

6. Set up the apparatus as the figure below. And ask your lab demonstrator to check.



7. Read the reading on burette (read to two decimal places, like 0.00 mL), and record it on a paper as **"V initial".**

8. Open the stopcock of the buret to add ~6 mL of NaOH. You will also see the solution in Erlenmeyer flask turns to pink color. Swirl the flask for 5 seconds, the pink color will quickly fade.

9. **Slowly** open the stopcock of the buret to add NaOH dropwise (like one drop per two seconds). Gently swirl the flask while adding NaOH. You will also see a faint pink color appear and quickly fade. Keep an eye on the buret reading, when it reaches 9 mL, close the stopcock.

10. The titration is now very close to the endpoint. You will slowly control the stopcock by adding only one drop at each time. Swirl the flask for 3 seconds after each adding. You will see the color begins to disappear more slowly. If there is a bit liquid stay on the buret tip, rinse it down with deionized water from a wash, this ensures that all of NaOH delivered from the buret ends up in the reaction mixture.

11. The equivalence point will reach when the faint pink color lasts for at least 30 seconds.

12. Read the reading on burette (read to two decimal places, like 10.00 mL), and record it on a paper as **"V final"**. Calculate the difference: $\mathbf{V_{(NaOH\ standard)}}$ **= "V final" – "V initial"**

13. Then, calculate the concentration of "HCl unknown":

$$M_{(NaOH\ standard)} \times V_{(NaOH\ standard)} = M_{(HCl\ unknown)} \times V_{(HCl\ unknown)}$$

Where $M_{(NaOH\ standard)} = 0.100$ mol/L
$V_{(HCl\ unknown)} = 10.00$ mL

$$0.100\ \text{mol/L} \times V_{(NaOH\ standard)} = M_{(HCl\ unknown)} \times 10.00\ \text{mL}$$

$$\therefore \boxed{\mathbf{M_{(HCl\ unknown)} = 0.100\ mol/L \times V_{(NaOH\ standard)} \div 10.00\ mL}}$$

For example, if $V_{(NaOH\ standard)} = 10.00 - 0.00 = 10.00$ mL,

then $M_{(HCl\ unknown)} = 0.100 \times 10.00 \div 10.00 = 0.100$ mol/L

14. Repeat steps 1 to 13 using 10.00 mL "Acetic Acid unknown" instead of "HCl unknown".

DISCUSSION

A. HCl unknown

Human stomach acid contains HCl, water, enzymes, and mucus. The main component is HCl. The pH of stomach acid typically ranges from 1 to 3, which equals HCl with concentration of 0.1 mol/L.

In this experiment, "**HCl unknown**" has similar concentration as human stomach acid. The theoretical value of its concentration is **0.100 mol/L**.

B. Acetic Acid unknown

Vinegar consists of acetic acid and water. It is normally produced by a two-step fermentation process. Sugars will be firstly converted to alcohol. Then, the alcohol will be fermented to acetic acid using bacteria. Typical household vinegar usually contains 4 – 7 % acetic acid, which is around 1.0 mol/L of acetic acid.

In this experiment, "**Acetic Acid unknown**" is ten times diluted to vinegar. The theoretical value of its concentration is also **0.100 mol/L**.

REFERENCES

1. Kolthoff, I. M. and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, 3rd ed., Macmillan, New York, Chapters 28, 29, 33, 34.

2. Skoog and West, Fundamentals of Analytical Chemistry, 2nd. ed., Holt, Rinehart, Winston, New York, Chapters 9, 11.